

Rapid Communication

A Novel Approach to Prepare Core/Shell Polymer Latex Particles with High Sulphonate Contents^{*}

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Abstract Crosslinked x-P(St-MAA) seed latex was first prepared *via* soap-free emulsion copolymerization of styrene (St) and methyl methacrylic acid (MAA) with divinyl benzene as crosslinker and ammonium persulfate as initiator, and x-P(St-MAA)/x-P(St-NaSS) core/shell latex particles were then synthesized through a novel seeded emulsion copolymerization of St and sodium styrene sulphonate (NaSS) in the presence of water-soluble crosslinker *N,N*-methylene bisacrylamide (BAA) using oil-soluble 2,2-azobis isobutyronitrile as initiator. TEM observation indicated that narrow dispersed core/shell latex particles were obtained, and element analysis showed that NaSS unit content in the whole particle and in the shell reached 22.8 wt% and 51.2 wt%, respectively.

Keywords: Sulphonate-containing particles; Seeded emulsion polymerization; Morphology; Core/shell.

INTRODUCTION

Sulphonate-containing polymers with good stability towards hydrolysis, oxidation, thermal degradation and high proton conductivity have drawn a lot of attentions of researchers in the last 3 decades^[1–6]. Due to their fascinating properties, they have some potential applications in biomedicine, optoelectronic and electronic devices, catalysts and polymer electrolyte membranes used in fuel cells^[2, 4, 7–9].

Sulphonate-containing polymer particles have attractive potential applications particularly in controlled release, delivery and enzyme immobilization. Matsumoto and co-workers prepared core/shell particles by crosslinking block copolymer micelles, and found that the sulphonate groups could be controlled in the shell or in the core part of the particles under specific conditions^[10–12]. But because of its complicated synthesis procedure including block polymer synthesis, self-assemble in the selected solvent, crosslinking of the micelle and post-treatment of the crosslinked micelle, this method was limited to prepare the core/shell particles in milligram scale.

Emulsion polymerization is a versatile technique in the preparation of functional polymeric particles with variable morphology such as core/shell and hollow latex particles in large scale^[13, 14]. Some conventional emulsion copolymerization approaches have been investigated to prepare poly(styrene-sodium styrene sulphonate) (P(St-NaSS)) latex particles, and the corresponding mechanisms have been proposed^[15, 16]. However, for the emulsion copolymerization of NaSS and St, because NaSS is water soluble and St is oil soluble, their incompatibility makes the emulsion copolymerization more complicated, and the concurrence of the homopolymerization of NaSS from homogeneous nucleation and the copolymerization of St and NaSS from

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micellar nucleation makes the conventional emulsion copolymerization impossible to prepare high sulphonate-containing P(St-NaSS) latexes. For example, Kim and his coworkers have synthesized P(St-NaSS) latexes *via* conventional batch, seeded batch and semi-continuous emulsion copolymerization, respectively, and found that no matter how much amount of NaSS was charged in the polymerization recipe, the content of NaSS units in the final latex copolymer could not exceed 2.6 wt%^[17, 18]. In our previous study, the NaSS unit content of the P(St-NaSS) latex particles have been increased obviously in the presence of anionic/nonionic complex emulsifier or in the ethanol/water reaction medium^[19, 20].

Since some of the properties such as proton conductivity mainly depend on the sulphonate content, how to increase sulphonate content is a key problem in the preparation of sulphonate-containing particles. In this work, a new approach as illustrated in Fig. 1 was used to prepare core/shell nanoparticles with high sulphonate contents, and influences of *N,N*-methylene bisacrylamide (BAA) on the particle size and its distribution, particle morphology as well as sulphonate content were investigated.



Fig. 1 Synthetic scheme of the x-P(St-MAA)/x-(St-NaSS) core/shell latex particles with high sulphonate contents *via* seeded emulsion copolymerization

MATERIALS AND EXPERIMENTS

All chemicals were of analytical grade from Alfa Aesar Co. and used as received unless noted. Styrene (St) and methyl methacrylic acid (MAA) were distilled under reduced pressure and stored in a refrigerator. Sodium styrene sulphonate (NaSS) and ammonium persulfate (APS) were recrystallized in water; 2,2-azobis isobutyronitrile (AIBN) was recrystallized in ethanol before use. Sodium dodecyl sulfate (SDS), divinyl benzene (DVB, 45%) and *N,N*-methylene bisacrylamide (BAA) were purchased from Fluka Co. Double distilled and deionized water was used throughout this work.

Crosslinked x-P(St-MAA) seed latex was prepared through soap-free emulsion copolymerization in a four-neck flask equipped with a reflux condenser, a mechanical stirrer and a thermometer in nitrogen atmosphere as follows: St 18.66 g, MAA 1.34 g, DVB 0.72 g and water 100 g were charged into the flask under stirring and the system was heated to 70 °C, then 0.336 g of APS dissolved in 25 g of water was introduced into the system in three steps with the ratio of 12/8/5 at the beginning, 2 h and 4 h of polymerization, and the total reaction time was 7 h.

Seeded emulsion copolymerization of St and NaSS was carried out in the four-neck flask in nitrogen atmosphere to prepare x-P(St-MAA)/x-P(St-NaSS) core/shell latex particles. A typical recipe was as follows: the seed latex 20.0 g (solid content: 13.2 wt%), SDS 0.068 g, AIBN 0.034 g, water 35.0 g, St 0.923 g, NaSS and BAA variable. In experiments, the seed latex and 10 g of water were first charged into the flask, then AIBN dissolved in St was added to swell the x-P(St-MAA) seed particles at room temperature for 3 h under gentle stirring. After that, the solution of NaSS, BAA and SDS in 25 g of water was introduced into the system, and the polymerization was performed at 70 °C for 10 h.

Hydrodynamic diameter (D_p^{DLS}) and its distribution (poly index) of the latex particles were determined by dynamic light scattering (DLS) method on a ZetaSizer 3000HS (Malvern, UK) at 25 °C. Number average diameter (D_p^{TEM}) and morphology of the dried seed and core/shell latex particles were characterized with a transmission electron microscope (TEM, Hitachi 800, JP).

In order to remove the water-soluble components in the core/shell latex products, about 20 mL of the original latex was dried first, and the resultant solid was then extracted with water in a Soxhlet' extractor for 48 h. The weight loss of the samples was recorded to express the crosslinking level of the core/shell latex particles.

The sulfur content of the extracted polymer samples was determined on a VISTA-MPX ACPOES elementary analyzer. Based on the sulfur content, the NaSS unit content in the whole particle and in the shell part was calculated, respectively.

RESULTS AND DISCUSSION

The soap-free emulsion copolymerization performed smoothly with the monomer conversion of 94.3%, and the stable seed latex with D_p^{DLS} of 274 nm and D_p^{TEM} of 170 nm was obtained. The TEM photo (Fig. 2a) exhibited that the seed latex possesses narrow particle size distribution, which accords with the poly index of 0.002 received from dynamic light scattering analysis.

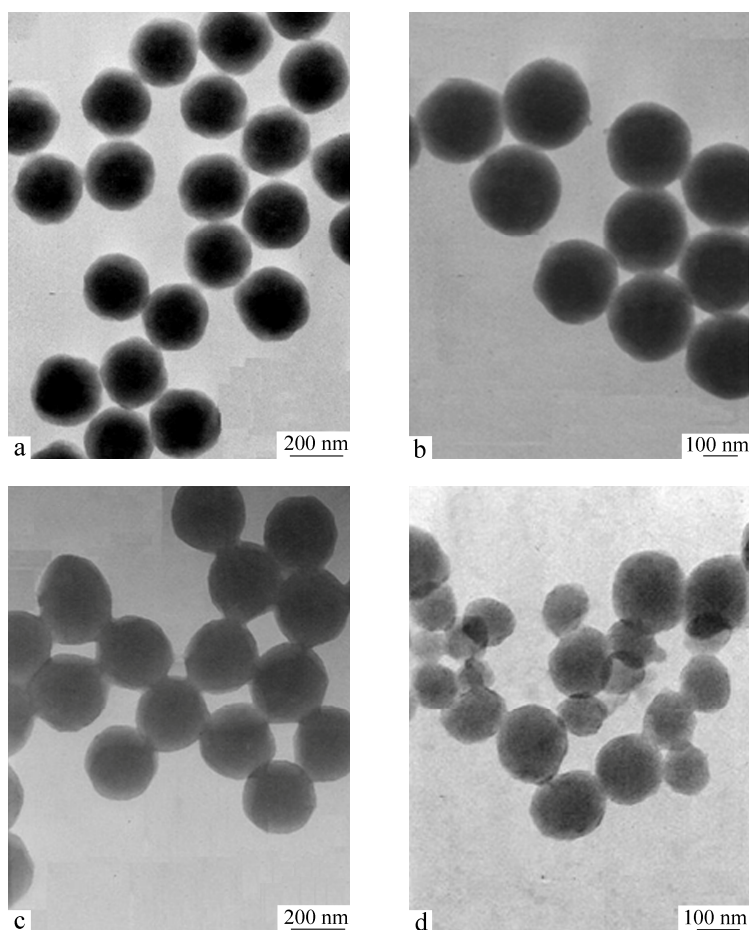


Fig. 2 TEM photos of the crosslinked x-P(St-MAA) seed latex (a) and the x-P(St-MAA)/x-P(St-NaSS) core/shell latexes prepared with different amount of BAA: (b) x-SF1, (c) x-SF2 and (d) x-SF3

In order to ensure that more NaSS molecules were polymerized onto the x-P(St-MAA) seed particles rather than in the aqueous phase, two measures were taken as follows: one is that oil-soluble initiator AIBN dissolved in St was introduced into the system to swell the seed particles before the polymerization to reduce the homopolymerizing probability of NaSS initiated in aqueous phase; the other is that water-soluble crosslinker BAA together with NaSS was charged into the system to make the shell polymer crosslinked to prevent the copolymer from dissolving in water.

Results showed that the seeded emulsion polymerization process was very sensitive to BAA, only 3 mol% BAA could lead to aggregation (sample x-SF3). When the BAA amount was less than or equal to 2 mol%

(samples from x-SF0 to x-SF2 in Table 1), narrow dispersed x-P(St-MAA)/x-P(St-NaSS) latex particles with D_p^{TEM} of about 250 nm were obtained (Figs. 2b and 2c).

Table 1. Influence of BAA amount on the core/shell latex particle size and its distribution

Sample	BAA/NaSS/St/(St+MAA in seed) (mol ratio)	D_p^{DLS} (nm)	Poly index	D_p^{TEM} (nm)
x-SF0	0/25/25/50	422.1	0.016	248
x-SF1	1/25/25/50	454.3	0.050	255
x-SF2	2/25/25/50	429.7	0.076	250
x-SF3	3/25/25/50	999.4	0.414	—

In order to verify the appropriate BAA amount that makes the shell polymer crosslinked efficiently, the core/shell latex products prepared with different amounts of BAA were extracted with water, and the results are listed in Table 2. It is clear that the found weight loss was much lower than its theoretical value for all of the samples; and as expected, increasing BAA amount could decrease the weight loss significantly, and 2 mol% of the crosslinker could decrease the weight loss to 7.33 wt% (sample x-SF2).

Table 2. Effect of BAA amount on the weight loss of the core/shell latex products in water extraction

Sample	Found (wt%)	Weight loss	
		Theo. (wt%) ^a	Found/Theo.
x-SF0	18.4	40.2	0.46
x-SF1	8.31	39.8	0.21
x-SF2	7.33	39.3	0.19
x-SF3	6.96	38.9	0.18

^a Assuming all of NaSS was polymerized to form homopolymer PNaSS which could be removed after extraction

As a control experiment, the x-P(St-MAA) seed latex product was also extracted with water under the same condition, and it was found that its weight loss was 5.00 wt%. The difference of weight loss between the seed latex product and the core/shell latex product (sample x-SF2) was only 2.33 wt%, indicating that the shell of core/shell latex particles was crosslinked efficiently by water-soluble BAA.

As above indicated, when 2 mol% of BAA to the total monomers was used in the core/shell latex preparation, the narrow dispersed x-P(St-MAA)/x-P(St-NaSS) latex with less weight loss in water extraction could be obtained. The sulfur content of the extracted core/shell latex product (sample x-SF2) was determined and found to be 3.54 wt%, and it could be calculated that the NaSS unit content in the whole latex product was 22.8 wt%. Since all of the sulphonate groups were in the shell layer, when the core materials were ruled out in calculation, the NaSS unit content in the shell polymer reached 51.2 wt%.

CONCLUSIONS

In summary, the narrow disperse x-P(St-MAA)/x-P(St-NaSS) core/shell latex particles with high sulphonate content in the shell were prepared *via* a novel seeded emulsion polymerization using oil-soluble AIBN as initiator and water-soluble BAA as crosslinker. The polymerization process, the weight loss of the core/shell latex product in water extraction and the NaSS unit content in the extracted core/shell latex product were significantly influenced by the BAA amount, and the appropriate amount of BAA to the total monomers was 2 mol%. When the NaSS/(St + MAA) mole ratio was 25/75 and BAA amount was 2 mol%, the NaSS unit content in the whole x-P(St-MAA)/x-P(St-NaSS) particle and in the shell was 22.8 wt% and 51.2 wt%, respectively.

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